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SELF-PROPAGATING CRYSTALLIZATION IN THE SYNTHESIS OF GLASS CERAMICS BASED ON ASH-SLAG WASTE

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The phenomenon of self-propagating crystallization (SC) is implemented in the synthesis of slag glass ceramics based on waste from the Kansk-Achinskii coal field, and the possibility of using SC as the process technique is demonstrated. The effect of a fluorite additive introduced into the batch in order to intensify the exothermic effect in SC sintering is investigated. It is demonstrated that using SC makes it possible to decrease the duration and general temperature of the process.

It is known that glass ceramics can be produced not only according to the glass technology, but, similarly to ceramics, can be obtained from glass powder of the corresponding chemical composition. Application of amorphous powders in ceramic and powder metallurgy technologies and in diffusion welding substantially raises sintering intensity and opens wide opportunities for the development of new materials with qualitatively new and improved characteristics. Porosity formed in this way, which generally is regarded as a defect, can be a positive factor, for instance in the development of heat-insulating and soundproof materials, filters, etc.

Technologies for the development of new structural materials can be based on the phenomenon of self-propagating crystallization (SC), which was discovered in studying the physicochemical properties of amorphous materials synthesized by the plasma spraying and melt chilling methods [1]. The SC mechanism is similar to self-propagating high-temperature synthesis (SHS). SC was studied on amorphous films of Ge, Bi, Yb, and (InCa)Sb [2–4]. Crystallization is initiated by a localized energy pulse and then propagates over the whole sample with a certain front velocity. The temperature of the crystallization front significantly exceeds the initial temperature of the sample. It is also established that SC can be initiated only in samples whose initial temperature exceeds a critical temperature T_0 . The principal role in the self-sustained nature of SC is played by the heat Q emitted as the material passes from the amorphous state to the crystalline state ($a \rightarrow k$ transition).

The necessary condition for SC is determined by the inequality

$$\beta Q > E,$$

where $\beta < 1$ is the thermal energy dissipation factor and E is the activation energy of the $a \rightarrow k$ transition.

We have developed a method for synthesis of porous glass ceramics from a glass powder based on ash generated in the combustion of brown coal from the Kansk-Achinskii coal field. The ash has the following composition (here and elsewhere in wt.%): 47 SiO₂, 7 Al₂O₃, 10 Fe₂O₃, 27 CaO, 5 MgO, and 1 (Na₂O + K₂O).

The samples were prepared according to the following scheme: batch preparation → glass melting → melt cooling in water → milling glass granulate into powder → molding → SC sintering.

The initial material was a batch that contained ash of the specified composition and an additive of fluorine-bearing mineral (fluorite CaF₂) for the purpose of raising heat emission in the $a \rightarrow k$ transition. The use of fluorides as crystallization catalysts is based on the fact that even small additions cause modifications in the glass, which in a second heating makes it possible to form fluorine-bearing seeds that facilitate crystallization of the matrix phase. The fluorine ion can be incorporated into the silicate glass structure, replacing the oxygen ion, since the sizes of fluorine and oxygen ions are similar (0.136 and 0.140 nm, respectively). However, their valences are not equal; therefore, to preserve electroneutrality, each oxygen ion requires two fluorine ions, which results in breaking of the volumetric Si–O–Si bonds in the silicon-oxygen tetrahedra and weakens the local Si–F bonds. Fluorine causes destruction of the glass lattice, which presumably is responsible for the tendency to form fluorine-containing groups as seeds in the second heating and for the preparation of glass components on the whole for crystallization [5]. Samples were prepared with CaF₂ additives equal to 5, 10, 15, and 20 wt.% of the ash weight. To decrease the temperature of batch melting, MgO in an amount of 20 wt.% of ash weight was used as a flux.

The batch was heated in an alundum crucible in an air atmosphere inside the furnace to a temperature of 1300°C with an exposure of 40 min. The melt was chilled by the thermal

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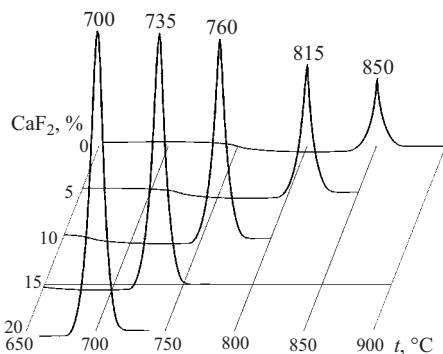


Fig. 1. Thermograms of samples.

shock method with discharge into water. Abrupt chilling of the melt made it possible to obtain glass granulate with a large reserve of internal energy.

The crystallization temperature of intermediate products was determined using the DTA method on a derivatograph (Fig. 1). Analysis of DTA curves indicates that an increase in CaF_2 content raises heat emission in the $\alpha \rightarrow k$ transition and lowers the temperature of crystallization.

Granulated glass was ground to a powder with a particle size below $80 \mu\text{m}$, mixed with a binder (7% polyvinyl alcohol), and compressed in a steel mold in the form of cylinders 20 mm in diameter and 40 mm high at a pressure of 30 MPa. Molded samples were placed in a furnace for drying for 1 h at 150°C .

The prepared samples were placed in a gradient furnace and sintered (Fig. 2). The temperature in the upper part of the furnace was automatically raised to the temperature of sample crystallization found from the DTA thermogram. After the upper layer of the sample was heated up to the crystallization temperature, an intense exothermic effect was visually observed: a cupola-shaped incandescent crystallization front appeared and moved along the sample from top to bottom. The thermal wave velocity was around $1.7 \times 10^{-4} \text{ m/sec}$, which was slightly higher in samples with a high content of CaF_2 . The reaction rate increases as well in the case of preliminary heating of samples and temperature rise inside the furnace. This is also indicated by the cupola shape of the crystallization front, which is a result of better heating of the sample from its lateral surface.

The phase composition of the materials, intermediate, and final products was monitored using a DRON-3 x-ray diffractometer (tube current 30 mA, voltage 30 kV). Figure 3 shows the diffraction patterns of granulated glass and of the crystallized material, which is represented by phases of helenite $\text{Ca}_2\text{Al}_2[\text{SiO}_7]$, okermanite $\text{Ca}_2\text{Mg}[\text{Si}_2\text{O}_7]$, and fassaite $\text{Ca}(\text{Mg}, \text{Fe}^{3+}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_6$. There is also a residual vitreous phase, which is evidenced by intensified peaks on the diffraction patterns after additional annealing of samples at the crystallization temperature.

The sample with 20% CaF_2 was analyzed to determine its density, porosity, and microhardness. The density of the compact material is 3 g/cm^3 and the density of the sample according to GOST 18898-73 is 2.36 g/cm^3 . The relative

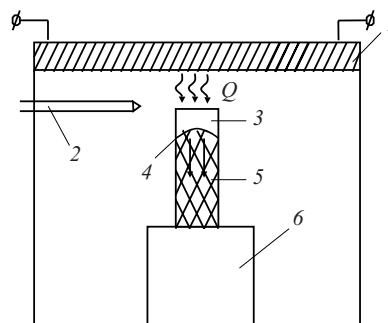


Fig. 2. Scheme of sample heating: 1) heater; 2) thermocouple; 3) crystallized part; 4) crystallization front; 5) amorphous part; 6) refractory support.

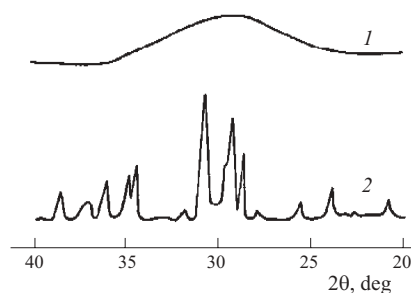


Fig. 3. Spectra of x-ray phase analysis of a sample with 20% CaF_2 additive: 1) amorphous state; 2) after crystallization.

density is 78.7%, and the total porosity 21.3%. The microhardness under loading of 1.96 N is at the level of 7500 MPa.

The performed studies suggest that SC can be used as a method for production of glass ceramic materials. This method decreases the duration (compared to the ceramic technology) and total temperature of heat treatment (compared to the traditional method of making glass ceramics). The use of this method makes it possible as well to regulate the ratio of the crystalline phase to the vitreous phase by applying the appropriate temperature schedule. It is noteworthy that SC has been implemented on the basis of inexhaustible material, i.e., ash-and-slag waste from the Kansk-Achinskii coal field, whose utilization is still a problem.

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